

## WHAT IS CLAIMED IS:

1. An improved process for the anionic polymerization of at least one vinylic monomer to form a branched polymer, comprising contacting, in the presence of an anionic initiator:
  - 5 (i) one or more anionically polymerizable vinylic monomers having the formula  $\text{CH}_2=\text{CYZ}$ , and
  - (ii) an anionic polymerization chain terminating agent of formula  $\text{CH}_2=\text{CZ-Q-X}$

wherein:

  - 10 Q is selected from the group consisting of a covalent bond, R, C(O), RC(O);  
Y is selected from the group consisting of R,  $\text{CO}_2\text{R}$ , CN,  $\text{NR}_2$ ;  
X is selected from the group consisting of halogen,  $\text{RSO}_3$ ;  
Z is selected from the group consisting H, R, CN;
  - 15 R is selected from the group consisting of unsubstituted and substituted alkyl, olefin, aryl, aralkyl, alkaryl and organosilicon groups, the substituents being the same or different and selected from the group consisting of carboxylic acid, carboxylic ester, hydroxyl, alkoxy and amino;
  - 20 wherein the improvement comprises obtaining higher yields of branched polymer, the polymer having dense branch upon branch architecture and polymerizable vinylic chain termini, employing steps I, III, VI and at least one of II, IV and V:
    - I. reacting (i) with an anionic initiator in a first step;
    - 25 II. decreasing the ratio of (i) to anionic initiator toward 1 ;
    - III. adding (ii) optionally with some (i) in a second step;
    - IV. selecting the rate of the (ii) addition, dependent on the reactivity of (ii);
    - V. increasing the ratio of (ii) to anionic initiator toward 1;
    - 30 VI. increasing the conversion of (i), (ii) and olefinic end groups from 70 toward 100 %; and
    - VII. optionally, converting anionic-growing end groups into non-polymerizable end groups.
  - 35 2. A process according to Claim 1 wherein in (i) Z = H or  $\text{CH}_3$ .

3. A process according to Claim 1 wherein in (i) Y = Ph or CO<sub>2</sub>R.
4. A process according to Claim 1 wherein in (i) Z = H and  
5 Y = Ph.
5. A process according to Claim 1 wherein in (ii) Q = PhCH<sub>2</sub> and X = Cl or Br.
- 10 6. A process according to Claim 1 wherein in (i) Z = H and Y = Ph, in (ii) Q = PhCH<sub>2</sub> and X = Cl or Br, and BuLi is used as an initiator.
7. A process according to Claim 1 employing step VII.
- 15 8. A process according to Claim 7 employing a chain-terminating agent that provides a non-polymerizable moiety.
9. A composition of matter comprising a polymer having a branch-upon-branch structure and optionally a polymerizable olefinic end group, having the structure:
- $$\begin{array}{c} Z & & B & & Z \\ | & & | & & | \\ A - (\text{CH}_2 - \text{C} - )_n (\text{CH}_2 - \text{C}-)_m (\text{CH}_2 - \text{C}-)_p \text{ QW} \\ | & & | & & | \\ Y & & Z & & Y \end{array}$$
- 25 where B =
- $$\begin{array}{c} Z & & B' & & Z \\ | & & | & & | \\ A - (\text{CH}_2 - \text{C} - )_n (\text{CH}_2 - \text{C}-)_m (\text{CH}_2 - \text{C}-)_p \text{ Q-} \\ | & & | & & | \\ Y & & Z & & Y \end{array}$$
- 30 wherein:
- B' = Y, B;
- m = 1 to 100, n = 0 to 100, p = 0 to 100, n+m+p ≥ 2;
- 35 and if m > 1, then the m insertions are consecutive or not consecutive;
- A = anionic initiator moiety selected from the group consisting of R;

Q is selected from the group consisting of a covalent bond, R,  
C(O), RC(O);

Y is selected from the group consisting of R, CO<sub>2</sub>R, CN, NR<sub>2</sub>;  
W is CZ = CH<sub>2</sub> or a non-polymerizable moiety;

5 X is selected from the group consisting of halogen, RSO<sub>3</sub>;

Z is selected from the group consisting of H, R, CN; and

R is selected from the group consisting of unsubstituted and  
substituted alkyl, vinyl, aryl, aralkyl, alkaryl and organosilanyl  
groups, the substituents being the same or different and

10 selected from the group consisting of carboxylic acids,  
carboxylic ester, hydroxyl, alkoxy, primary amino and  
secondary amino.

10. A composition according to Claim 9 wherein A = butyl, Z  
15 = H, and Y = Ph, and Q = C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>.

11. A composition of Claim 10 wherein W is CZ = CH<sub>2</sub>.

12. A composition of Claim 10 wherein W is a non-  
20 polymerizable moiety.

13. A composition of Claim 12 wherein W is H.